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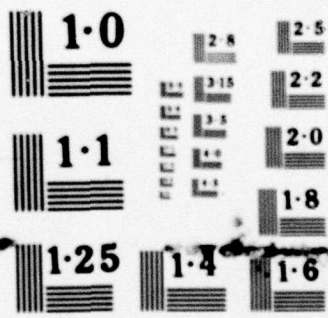
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CHARGED ATMOSPHERIC CONGLOMERATES: ROLE OF NEGATIVE IONS  
IN HETEROMOLECULAR NUCLEATION; THE PROPERTIES OF SMALL  
CLUSTERS AND ATMOSPHERIC IONS

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A. W. Castleman, Jr.

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21. ABSTRACT (Continue on reverse side if necessary and identify by block number) During recent years, there has been an enormous growth of interest in the properties of small particles and in the mechanisms by which they are formed. This has been due partly to the realization that findings in this field can contribute to an understanding of a very wide range of fundamental problems concerned with phase transitions, the formation, structure and reactivity of surfaces, the nature and stability of the aerosol state, and even		

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20. Abstract (continued)

the kinetics of association and unimolecular reactions, and solvation phenomenon. Further impetus has also arisen because of the larger number of applied areas to which the results have a direct bearing including the atmospheric sciences, obscuration, combustion research, and catalysis to mention just a few. In all but one of these areas the system of interest is that comprised of particles dispersed in the gas phase commonly termed an aerosol.

The research program undertaken in our laboratory was directed to a study of the fundamentals of nucleation about negative ions, with particular attention to an elucidation of the structure of small clusters, and the role of chemical bonding in establishing their stability. Using a new high pressure mass spectrometric technique, a systematic investigation of the bond energies and entropies of numerous ligand-negative ion complexes were determined. Concurrent theoretical work on the bonding of small complexes and ion-induced nucleation was also undertaken. The results have led to a more complete understanding of nucleation phenomena, and especially of the importance of cluster structure in the development of surfaces and in effecting phase transformations. In addition, the work has led to a clarification of some recent atmospheric observations reported in the literature.

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## TABLE OF CONTENTS

Summary of Findings	1
List of Publications	16
Invited Seminars and Talks	18
List of Participating Scientific Personnel	21
Bibliography	22

### APPENDIX A

"Nucleation and Molecular Clustering About Ions"

### APPENDIX B

"The Properties of Ion Clusters and Their Relationship to Heteromolecular Nucleation"

### APPENDIX C

"Statistical Mechanics of Nucleation and Early Stages of Aerosol Growth: Implications of Recent Experimental Findings"

### APPENDIX D

"Studies of Ion Clusters: Relationship to Understanding Nucleation and Solvation Phenomena"

### APPENDIX E

"The Properties of Clusters in the Gas Phase: Hydration Complexes of  $\text{CO}_3^-$  and  $\text{HCO}_3^-$ "

### APPENDIX F

"Atmospheric Negative Ion Hydration Derived from Laboratory Results and Comparison to Rocket-Borne Measurements in the Lower Ionosphere"

### APPENDIX G

"The Properties of Clusters in the Gas Phase: IV. Hydration Complexes of  $\text{H}_2\text{O}$  and  $\text{HNO}_x$  Clustering on  $\text{NO}_x^-$ "

### APPENDIX H

"A Reconsideration of Nucleation Phenomena in Light of Recent Findings Concerning the Properties of Small Clusters, and a Brief Review of Some Other Particle Growth Processes"



### Summary of Findings

Support from the U. S. Army Research Office commenced on 10 June 1976 for a grant entitled "Charged Atmospheric Conglomerates: Role of Negative Ions in Heteromolecular Nucleation; the Properties of Small Clusters and Atmospheric Ions." The early period of the grant was devoted to reconstructing, with numerous modifications, an apparatus moved to the University of Colorado when the principal investigator accepted a position there. Following necessary testing procedures, an experimental program devoted to providing the molecular basis for understanding the stability of negative ion clusters was begun. Related theoretical work on ion-cluster structure, and for assessing the validity of conventional treatments of heteromolecular nucleation, was also done concomitantly.

The results of this research have led to the publication of eight papers (currently in print or in press) attached as Appendices A-H, presentations at 39 meetings and seminars, and results for six other journal articles which are now in preparation. Since the results are detailed in the attached papers, only a very brief summary of the findings is given here. In accordance with the original proposal, the work was directed largely to systems of interest in the upper atmosphere.

#### 1. Studies of the Bonding of Negative Ion Clusters

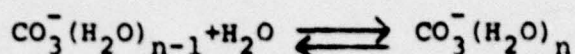
It is well known that both natural events, such as solar flares, as well as manmade ones such as a nuclear burst, can cause atmospheric electron densities and levels of ionization to be increased to values several orders of magnitude higher than those

of the unperturbed atmosphere. Since the propagation of directed electromagnetic radiation (i.e., radar, radio signal, and optical signals) is influenced by the intensity of these levels, a determination of the chemical and physical processes controlling the rate of return to normal atmospheric conditions was deemed of considerable importance so that the effect of these perturbations on communication could be properly assessed.

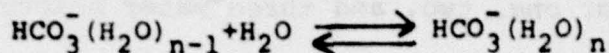
Although considerable attention had been given to a study of the homogeneous chemical reactions and physical charge exchange processes which might operate in the atmosphere, by comparison very little was known about the processes associated with clusters, conglomerates, and small aerosols. Of particular interest is an understanding of the properties and fate of negative ions. Mass spectrometer measurements made in the upper atmosphere by Krankowsky, et al.<sup>(1)</sup> and Narcisi<sup>(2)</sup> have showed the existence of an abundance of various negative ion clusters. The findings of Krankowsky and coworkers showed  $\text{CO}_3^-$  to be a major ion, followed by  $\text{HCO}_3^-$  and  $\text{NO}_3^-$ ; the data also indicated the existence of hydration complexes of these, as well as the presence of  $\text{CO}_4^-$ , and  $\text{O}_2^-(\text{H}_2\text{O})_2$ , and perhaps  $\text{Cl}^-$  and  $\text{NO}_2^-\cdot\text{HNO}_2$ . Somewhat in conflict were the results of Narcisi who reported the tentative identification of  $\text{NO}_3^-(\text{H}_2\text{O})_n$  ( $n=0-8$ ),  $\text{CO}_3^-(\text{H}_2\text{O})_2$ , and  $\text{CO}_4^-$ . The latter believes that  $\text{Cl}^-$  and  $\text{NO}_2^-$  might originate from rocket contamination, but this suggestion is disputed by Krankowsky and Arnold.

In order to provide the data necessary for interpreting the stability of these complexes, an investigation of the thermodynamic properties of  $\text{CO}_3^-$  and  $\text{HCO}_3^-$  complexes with water was first undertaken. Specifically, extensive studies were made of the reaction:





with  $n$  ranging from 1 to 3, and



with  $n$  ranging from 1 to 4. Experiments were performed over a wide range of pressures, temperatures, and electrical field energies and it was established that equilibrium was indeed attained in the reaction cell. The technique, experimental details, and results are detailed in Appendix E. From measurements of the temperature dependencies of the equilibrium constants, both enthalpies and entropies were derived for the reactions. The results for reaction (1) are  $-\Delta H_{n-1,n}^0 = 14.1, 13.6, \text{ and } 13.1 \text{ kcal/mole}$  and  $-\Delta S_{n-1,n}^0 = 25.2, 29.6, \text{ and } 32.5 \text{ e.u.}$  for  $n=1$  to 3, respectively. For reaction (2) the respective enthalpy values are  $-15.7, -14.9, -13.6, \text{ and } -13.4 \text{ kcal/mole}$ ; the corresponding entropies are  $-24.1, -29.1, -30.2, \text{ and } -33.3 \text{ e.u.}$

An interesting finding is that the thermodynamic properties of the  $\text{CO}_3^-$  hydrates nearly merge with those of  $\text{HCO}_3^-$  of one less cluster size, beyond that of the first cluster of  $\text{CO}_3^-$ . Of particular importance is the fact that the enthalpies of hydration do not readily approach, asymptotically, the heat of condensation for  $\text{H}_2\text{O}$  as is often the case for positive ions. (See Appendix E, Figure 5). Therefore, the hydration of these negative ions is stronger than those of many analogous simple positive ions which do display this tendency. This gives credence to the rocket borne mass spectrometric findings of Arnold and Krankowsky regarding the importance of  $\text{CO}_3^-$  and  $\text{HCO}_3^-$  hydrates in the mesosphere. Details are discussed in Appendix F. As an aid in understanding the bonding resulting from hydration of these ions, approximate

quantum-mechanical molecular orbital calculations were performed with the CNDO/2 method for one, two, and three water molecules bound to  $\text{HCO}_3^-$ . Unlike the situation for positive ions, hydration complexes of negative ions develop through bonding of a hydrogen atom to the ion.

Intense interest also exists in the ions  $\text{NO}_2^-$  and  $\text{NO}_3^-$ , and we have completed studies of their interaction with  $\text{H}_2\text{O}$ , as well as  $\text{NO}_2^-$  with  $\text{HNO}_2$ ,  $\text{CO}_2$  and  $\text{SO}_2$ , and  $\text{NO}_3^-$  with  $\text{HNO}_3$ . Results of  $\text{NO}_x^-$  bonded with  $\text{H}_2\text{O}$  and  $\text{HNO}_x$  are discussed in Appendix G. (See Figures 1, 2, 3 and 4 (in the Appendix) for the equilibrium constants determined at a wide variety of temperatures.

Recent data acquired in our laboratory for the bond energies and entropies of the various negative ion cluster reactions are given in Table I, along with data for the hydration complexes of  $\text{CO}_3^-$  and  $\text{HCO}_3^-$  for comparison. The importance of the nature of the ligand on its ability to bond to negative ions, and particularly with regard to establishing a stable cluster species, is seen by comparing data for a number of different ligands bonded to one ion. Referring to Figure 1, equilibrium constants for a number of ligands bonded to  $\text{NO}_2^-$  are seen to be greatly different.

Significant differences are also observed in the case of various ions bound to a single ligand. An example is given in Figure 2 which is a plot, versus reciprocal temperature, of the logarithm of the equilibrium constants of  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_2^-$  and  $\text{SO}_3^-$  bonded with  $\text{SO}_2$ . On this basis, complexes of  $\text{SO}_2$  with  $\text{Cl}^-$  and  $\text{NO}_2^-$  should be especially important in regions where these parent ions exist; however, complexes with  $\text{SO}_3^-$  are unlikely to be



TABLE I

THERMODYNAMIC PROPERTIES OF NEGATIVE ION CLUSTERS  
RECENTLY MEASURED IN OUR LABORATORY

$A^- B_n + B \xrightleftharpoons{M} A^- B_{n+1}$									
$-\Delta H^\circ_{n, n+1}$ (kcal/mole)						$-\Delta S^\circ_{n, n+1}$ (gibb/mole)			
Ligand	ion	(0,1)	(1,2)	(2,3)	(3,4)	(0,1)	(1,2)	(2,3)	(3,4)
H <sub>2</sub> O	Cl <sup>-</sup>	14.9	12.6	11.5	10.9	19.7	20.5	22.4	24.8
	I <sup>-</sup>	11.1	9.9	9.3		19.3	20.3	21.0	
	CO <sub>3</sub> <sup>-</sup>	14.1	13.6	13.1		25.2	29.6	32.5	
	HCO <sub>3</sub> <sup>-</sup>	15.7	14.9	13.6	13.4	24.1	29.1	30.2	33.3
	NO <sub>2</sub> <sup>-</sup>	15.2	13.6	11.7	11.6	23.8	26.4	25.8	29.0
	NO <sub>3</sub> <sup>-</sup>	14.6	14.3	13.8		25.0	30.3	33.2	
CO <sub>2</sub>	Cl <sup>-</sup>	8.0				19.6			
	I <sup>-</sup>	5.6				18.2			
	CO <sub>3</sub> <sup>-</sup>	7.1				21.8			
	NO <sub>2</sub> <sup>-</sup>	9.3				24.2			
	SO <sub>3</sub> <sup>-</sup>	6.5				20.7			
SO <sub>2</sub>	Cl <sup>-</sup>	21.8	12.3	10.0	8.6	23.2	22.7	23.1	23.2
	NO <sub>2</sub> <sup>-</sup>	25.9	9.0	6.6		36.8	16.8	13.4	
	SO <sub>2</sub> <sup>-</sup>	24.0				33.8			
	SO <sub>3</sub> <sup>-</sup>	13.3				18.9			
	I <sup>-</sup>	12.9	10.1	9.2		20.2	21.6	24.7	

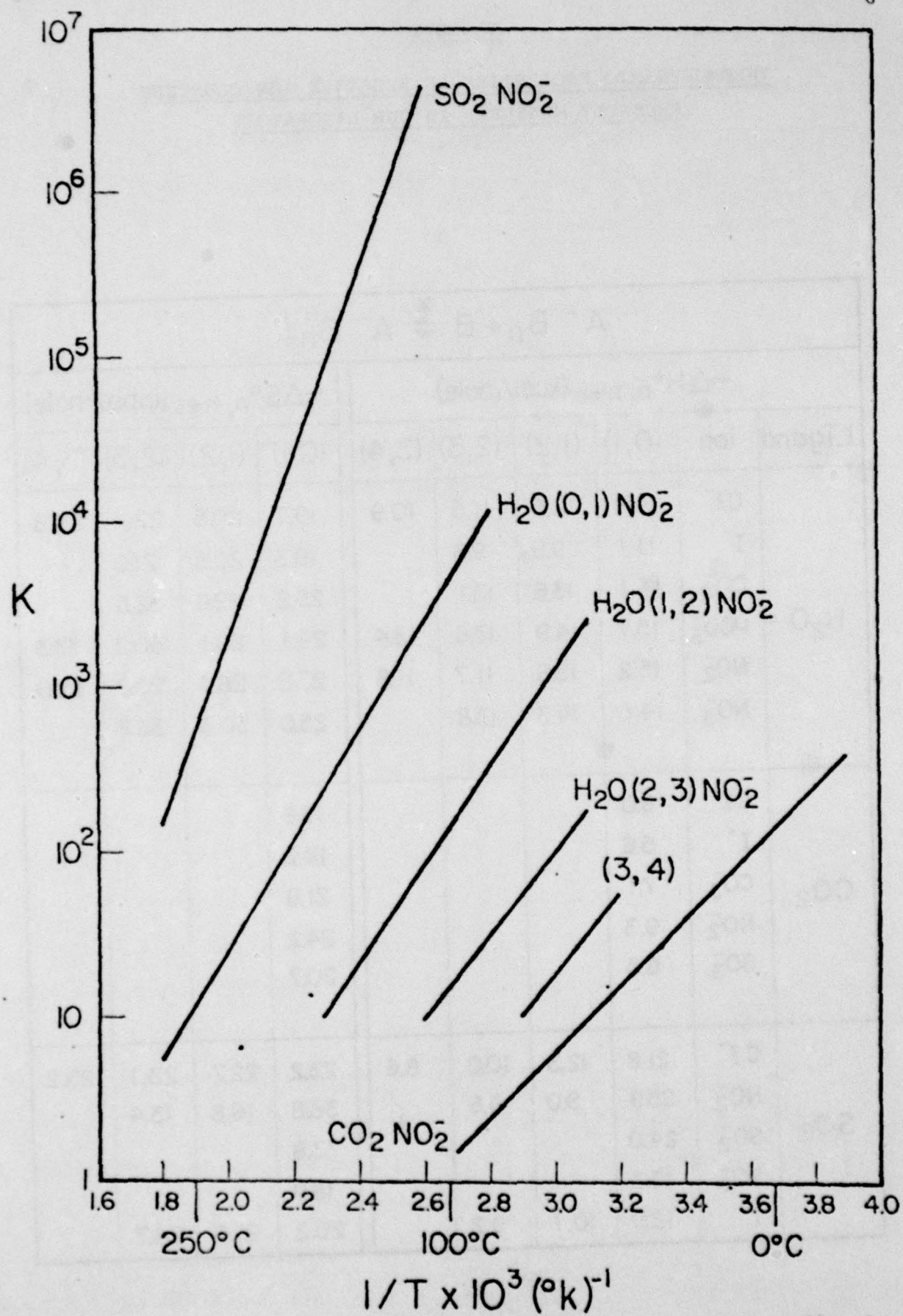


Fig. 1



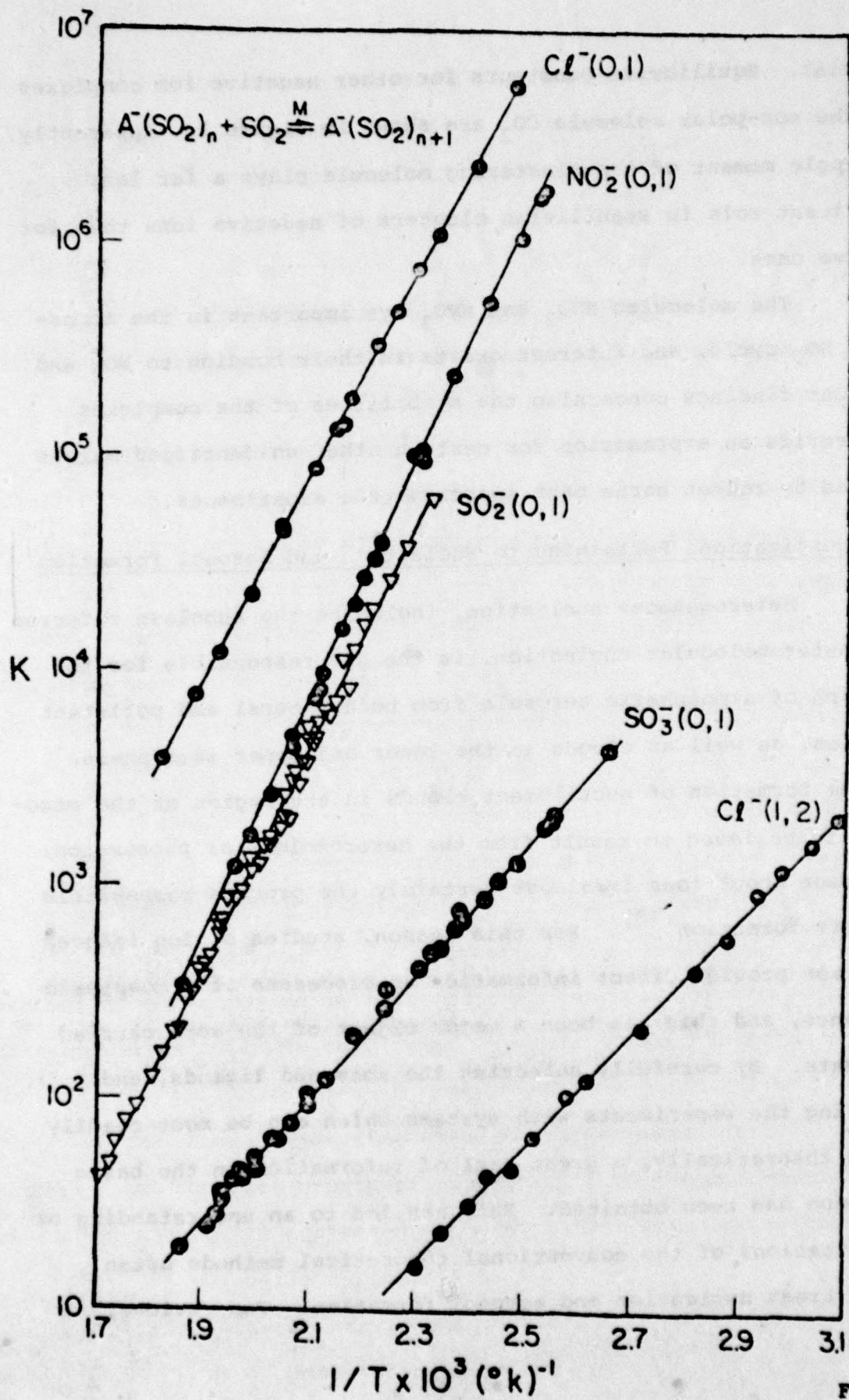


Fig. 2

important. Equilibrium constants for other negative ion complexes with the non-polar molecule  $\text{CO}_2$  are shown in Figure 3. Apparently, the dipole moment of the clustering molecule plays a far less significant role in stabilizing clusters of negative ions than for positive ones.

The molecules  $\text{HNO}_2$  and  $\text{HNO}_3$  are important in the atmospheric  $\text{NO}_x$  cycle, and interest exists in their bonding to  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . Our findings concerning the stabilities of the complexes also provide an explanation for certain other unidentified masses detected by rocket borne mass spectrometric experiments.

## 2. Investigations Pertaining to Nucleation and Aerosol Formation

Heterogeneous nucleation, including the subclass referred to as heteromolecular nucleation, is the one responsible for the formation of atmospheric aerosols from both natural and pollutant molecules, as well as clouds in the lower and upper atmosphere. Even the formation of noctilucent clouds in the region of the mesosphere is believed to result from the heteromolecular phenomenon; nucleation about ions is almost certainly the process responsible for their formation (3). For this reason, studies of ion induced nucleation provide direct information on processes of atmospheric importance, and this has been a major object of the work carried out to date. By carefully selecting the ions and ligands, and conducting the experiments with systems which can be most readily treated theoretically, a great deal of information on the basic phenomenon has been obtained. This has led to an understanding of the limitations of the conventional theoretical methods often used to treat nucleation and aerosol formation. Two reviews,



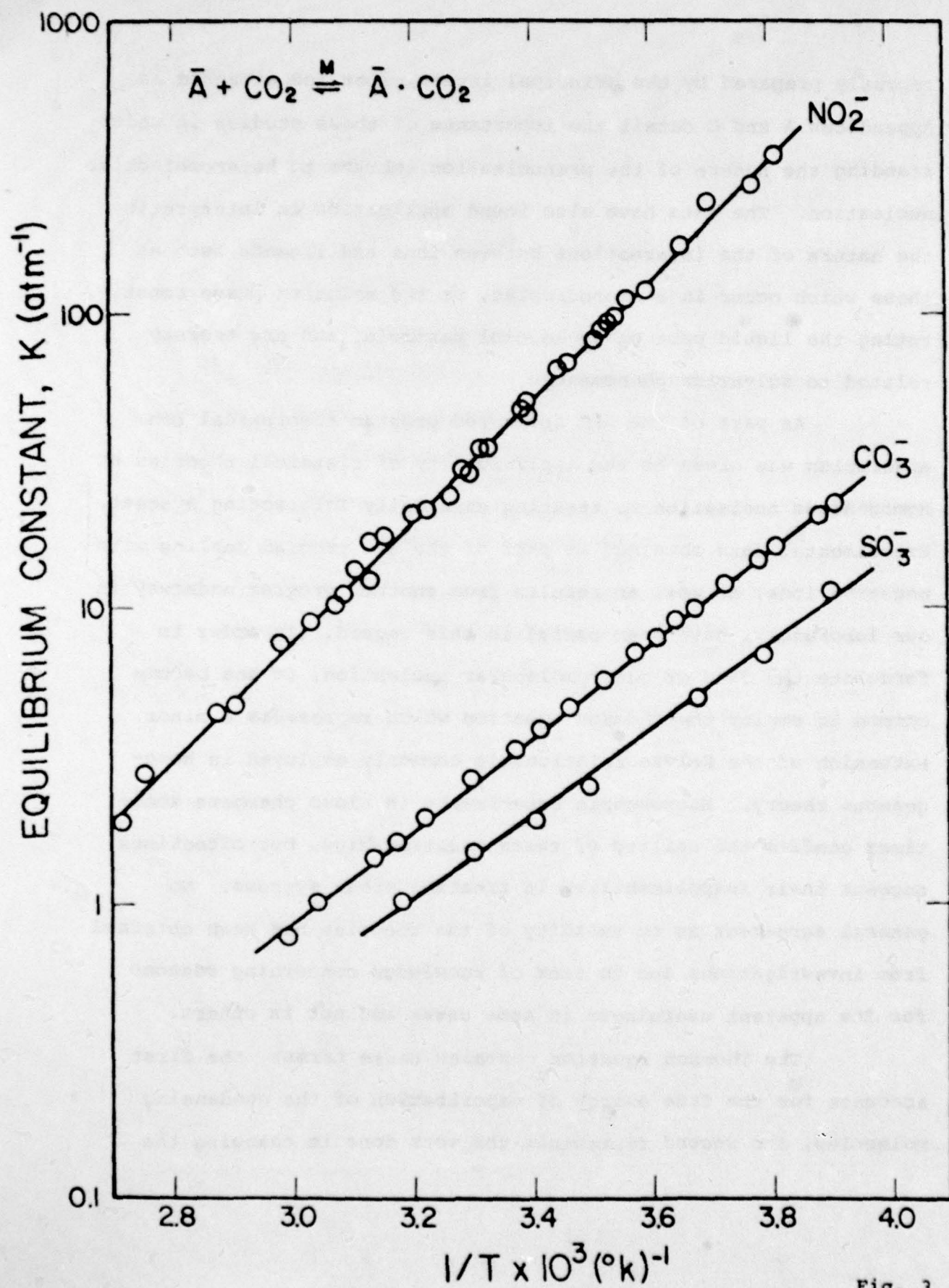


Fig. 3

recently prepared by the principal investigator and attached as Appendices A and C detail the importance of these studies in understanding the nature of the prenucleation embryos to heteromolecular nucleation. The data have also found application in interpreting the nature of the interactions between ions and ligands such as those which occur in a microdroplet, or the solution phase constituting the liquid part of an aerosol particle, and are thereby related to solvation phenomenon.

As part of the ARO sponsored program theoretical consideration was given to the applicability of classical theories of homogeneous nucleation to treating chemically interacting systems. Experimental data obtained as part of the ARO program dealing with negative ions, as well as results from another program underway in our laboratory, have been useful in this regard. In order to formulate the rate of heteromolecular nucleation, it has become common to employ the Thomson equation which represents a minor extension of the Kelvin relationship commonly employed in homogeneous theory. Macroscopic experiments in cloud chambers sometimes confirm the utility of these relationships, but oftentimes suggest their inapplicability in treating other systems. No general agreement as to validity of the theories has been obtained from investigations due to lack of knowledge concerning reasons for its apparent usefulness in some cases and not in others.

The Thomson equation contains three terms: the first accounts for the free energy of vaporization of the condensing molecules, the second represents the work done in changing the



surface area upon condensation of additional molecules about an ion cluster, and the third accounts for the change in field energy due to the condensation of a dielectric film (constant  $\epsilon$ ) about the ion. All of the capillarity approximations implicit in the use of the Kelvin equation for homogeneous nucleation are involved in the use of the Thomson equation; the nature of an ion is expressed only by its ionic radii. Consideration of the range of validity of the equation is instructive in developing an understanding of nucleation about ions and in deciding what terms must be sought in quantitatively accounting for the differences which various ions display in their ability to promote nucleation.

An expression for the free energy change per molecule,  $\Delta G_{n-1,n}$ , was readily developed by taking the derivative of the Thomson equation with respect to radius; derivative with respect to temperature enables an evaluation of entropy. Enthalpy (proportional to bond energy) is then obtained by substitution of these values into well known thermodynamic relationships. (Refer to Equations 3 and 11, Appendix B).

It is recognized that nucleation will not occur at supersaturations below 100%, and this is borne out by our calculations made for an ion-water system and shown in Figure 1. (See Appendix B) Here, the energy barrier to nucleation,  $\Delta\phi$ , is plotted versus cluster number  $n$  for varying ratios of  $\ln p/p_\infty$ , where  $p$  is the partial pressure of the condensing vapor and  $p_\infty$  the pressure above a surface with an infinite radius of curvature. The closed triangular points represent a saturated system where the energy barrier is effectively infinite; the minimum at cluster

size 10 represents the most abundant ion-cluster at this concentration of condensable vapor. At higher pressure ratios (supersaturation values), the barrier becomes finite and the size of the critical cluster decreases. At a logarithmic ratio of 1.2, a barrier no longer exists, and at higher supersaturation values nucleation becomes kinetically controlled.

This is consistent with a purely kinetic formulation of nucleation which was developed during the course of the work. (See Appendix B, Figure 2) The kinetics of cluster breakup (evaporation,  $k_r$ ) are plotted along with the forward (clustering,  $k_f$ ) rate in terms of its product with the concentration of the condensing molecule expressed by  $[A]$ . The intersection of the forward and reverse curves at small cluster sizes gives rise to a stable small cluster distribution. At  $[A]=1$ , corresponding to 100% saturation, no curve crossing occurs at finite cluster sizes; nucleation (curve crossing) results only at higher (super) saturations. The kinetically controlled regime indicated by the calculations shown in Figure 1 would then be represented by the case where the forward curve lies above the reverse one in Figure 2. Clearly, a complete understanding of nucleation requires a consideration of both reaction kinetics and the energy barrier to nucleation.

Pertinent to the problem of the validity of the Thomson equation is the degree to which this expression reproduces the requisite thermodynamic properties of the ion clusters. Two systems have been particularly revealing in this regard. One concerns the clustering of water to the alkali metal ions and  $Sr^+$ ,



while the other system is the isoelectronic molecule ammonia clustered to similar ions. Utilizing the appropriate derivatives of the Thomson equation we have compared the predicted with the experimental thermodynamic properties deduced from ion clustering studies.

In all cases the Thomson equation, and requisite derivatives thereof, have been shown to well represent the enthalpy for successive clustering of water and ammonia to ions of both open and closed electronic configuration. Likewise, considering the entropies for the clustering of water molecules, there is also a reasonable correspondence between the values predicted by the Thomson equation and those derived experimentally for both positive and negative ions. (See Figure 4 in Appendix D). However, a consideration of the entropy for ammonia clustering about the alkali metal ions reveals a great discrepancy between theory and experiment.

Referring to Figure 6 (Appendix B), it can be seen that at cluster sizes in the neighborhood of 4 or 5 there is a significant departure between the predicted and experimentally derived entropy values. Not only is the departure relatively large at this degree of clustering, but it is apparent that the trend is toward an even greater discrepancy with increasing cluster size. Clearly, the classical formulations do not hold for all nucleating systems. This finding is important in that it reveals, from a molecular point of view, reasons why certain systems have been found to be reasonably well represented by the energy barrier predicted by the Thomson equation while others display considerable departure. From the molecular clustering experiments it is

now apparent that this discrepancy is in fact a result of the nature of the structure of the prenucleation embryos to ion induced nucleation. The Thomson equation, by its very nature, implies a disordered liquid-like structure. In contrast, the experimental data for entropy values at small cluster sizes are seen to be quite negative, becoming more so with successive clustering. This implies that the small ion clusters have a relatively ordered structure, which provides a qualitative picture of the reasons why the Thomson equation is not valid for certain systems. It is interesting to note that no variation in the dielectric constant can give accord between the predicted and the experimental entropy values. But, an upward adjustment of the surface tension for the ion containing droplets with decreasing droplet radius was found to give somewhat better agreement. A proper formulation of surface tension for a droplet containing an ion immersed in a dielectric, awaits theoretical attention.

Consideration has also been given to the utility of the data in interpreting and quantifying the interactions between ions and ligands in the aqueous phase such as that associated with a micro-droplet aerosol phase. Details are given in Appendices D and G. By employing the high pressure mass spectrometric technique developed in our laboratory, we have been able to study the individual interactions at selected degrees of hydration. Thereby, detailed determination of bonding and the mechanisms and rates of reactions can be obtained for ready comparison with theory. Such data have not generally been attainable from studies typically performed in bulk solution, and their utility in interpreting processes involving aerosols has been limited. As



detailed in Appendix G, a particularly important result of the present work concerns the discovery of an unexpectedly simple correlation which relates cluster bond energy to bulk phase hydration energy, as a function of cluster size. Despite its simple form, it has been found to be valid for every negative ion hydration reaction for which data are available.

# LIST OF PUBLICATIONS

- "The Heats of Formation of  $\text{SO}_2\text{Cl}^-$  and  $(\text{SO}_2)_2\text{Cl}^-$ "; (with R. G. Keesee) Communications to the Editor, J. Amer. Chem. Soc. (submitted).
- "Evidence for Structures in Large Gas Phase Clusters Involving  $\text{H}_2\text{O}$ "; (with B. Kay and V. Hermann) J. of Chem. Phys. (submitted).
- "A Model for the Self-Stabilization of Charged Water Clathrates"; (with P. M. Holland) J. of Chem. Phys. (submitted).
- "A Reconsideration of the Theory of Capture Cross Sections for Ion-Molecule Reactions"; (with E. Hsieh) J. of Chem. Phys. (submitted).
- "The Properties of Clusters in the Gas Phase: IV. Hydration Complexes of  $\text{H}_2\text{O}$  and  $\text{HNO}_x$  Clustering on  $\text{NO}_x$ ; (with N. Lee and R. G. Keesee) J. of Chem. Phys. (submitted).\*
- "Statistical Mechanics of Nucleation and Early Stages of Aerosol Growth: Implications of Recent Experimental Findings"; J. of Aerosol Science, 10, pp. 183-185 (1979).\*
- "Studies of Ion Clusters: Relationship to Understanding Nucleation and Solvation Phenomena"; NATO Advanced Study Institute, "Kinetics of Ion Molecule Reactions," P. Ausloos, Ed., Plenum Press, N.Y. (1979), p. 295.\*
- "Atmospheric Negative Ion Hydration Derived from Laboratory Results and Comparison to Rocket-Borne Measurements in the Lower Ionosphere"; (with R. G. Keesee and N. Lee) J. of Geophysical Res., 84, 3719 (1979).\*
- "Nucleation and Molecular Clustering About Ions," Advances in Colloid & Interface Science "Nucleation"; A. Zettlemoyer, Ed., Elsevier Press, Oxford, England, 10 (1979), pp. 73-128.\*
- "The Properties of Clusters in the Gas Phase: III. Hydration Complexes of  $\text{CO}_3$  and  $\text{HCO}_3$ ; (with R. G. Keesee and N. Lee) J. Amer. Chem. Soc., 101 (10), 2599 (1979).\*
- "The Properties of Clusters in the Gas Phase: II. Ammonia About Metal Ions"; (with P. Holland, D. Lindsay and K. Peterson) J. Amer. Chem. Soc., 100, 6039 (1978).
- "The Properties of Clusters in the Gas Phase: I. Ammonia About  $\text{Bi}^+$ ,  $\text{Rb}^+$ , and  $\text{K}^+$ "; Chem. Phys. Lett., 53, 560 (1978).
- "Gas Phase Complexes: Considerations of the Stability of Clusters in the Sulfur Trioxide-Water System"; (with P. Holland) Chem. Phys. Lett., 56, 511 (1978).



"The Properties of Ion Clusters and Their Relationship to Heteromolecular Nucleation"; (with P. Holland and R. G. Keese), J. of Chemical Physics, 68, 1760 (1978).\*

"Analytical Studies for the U. S. Environmental Protection Agency"; Vol. III, Research and Development in the Environmental Protection Agency Report of the Environmental Research Assessment Committee (John Neuhold, Chairman), Commission on Natural Resources, National Academy of Sciences (1977), Washington, D.C.

"Analytical Studies for the U. S. Environmental Protection Agency"; Fates of Pollutants: Research and Development Needs; Panel on Fates of Pollutants, Chairman of Environmental Research Assessment Committee (January, 1977).

"Kinetics of the Association Reaction of  $\text{SO}_2$  with the Hydroxyl Radical," (with I. N. Tang) J. Photo Chem., 6, 349 (1976/1977).

"Role of Ions in Heteromolecular Nucleation"; Colloid and Interface Science, Vol. II, Aerosols, Emulsions and Surfactants, Ed. M. Kerker, Academic Press, P. 305 (1976).

"Aerosols in the Atmosphere: Their Origin and Role in Heterogeneous Processes"; Atmospheric Aerosols: Their Optical Properties and Effects, pp. MCl-1 to MCl-2, NASACP-20004 (1976).

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#### OTHER PUBLICATIONS IN PREPARATION REPORTING RESULTS FROM ARO SPONSORED RESEARCH

"Recent Advances in Ion Cluster Research," Endeavor, Ed. Treavor I. Williams, Pergamon Press, Limited, Oxford, England.

"The Gas-Phase Hydration of  $\text{Cl}^-$  and  $\text{I}^-$ ," (with R. G. Keese) J. of Amer. Chem. Soc.

"Properties of Clusters in the Gas Phase: V. Sulfur Dioxide and Carbon Dioxide Associated onto Negative Ions," (with R. G. Keese) J. of Chem. Phys.

"Gas Phase Complexes and Their Relationship to Solvation Phenomenon," (with N. Lee and R. G. Keese) J. of Chem. Phys.

"The Bonding of Sodium Ion to Dimethoxyethane," (with K. I. Peterson) J. of Amer. Chem. Soc.

"Aerosol Formation: Theoretical Considerations in Light of Recent Experimental Findings," J. of Aerosol Science.

## INVITED SEMINARS AND TALKS

"A Supersonic Molecular Beam Study of Homomolecular and Heteromolecular Aqueous Cluster Formation" (abstract); (with B. D. Kay, V. Hermann) American Chemical Society's Annual Meeting, Washington, D.C., September 9-14, 1979.

"The Gas Phase Clustering of Water, Sulfur Dioxide, and Carbon Dioxide onto Negative Ions" (abstract); (with R. G. Keese, N. Lee) American Chemical Society's Annual Meeting, Washington, D.C., September 9-14, 1979.

"Clustering of Water Vapor on Ions and Neutral Molecules"; (abstract) Atmospheric Water Vapor Workshop, Vail, Colorado, September 11-13, 1979.

"Studies of Small Clusters: Relationship to Understanding Nucleation and Solvation"; invited speaker to Gordon Conference on Chemistry and Physics of Liquids, Holderness School, Holderness, New Hampshire, August 13-17, 1979.

"Assessment of our Understanding of Fine Particle Formation by Nucleation in the Atmosphere"; invited speaker to Gordon Research Conference on Environmental Sciences - Air, New Hampton School, New Hampton, New Hampshire, June 18-22, 1979.

"Investigations of the Stability and Structure of Neutral and Ionized Clusters: Their Role in Understanding Nucleation Phenomena"; Presiding Chairman, Aerosols--Symposium on Nucleation Honoring A. C. Zettlemoyer, 53rd Colloid and Surface Science Symposium, University of Missouri-Rolla, June 11-13, 1979.

"Position Paper on Heterogeneous Reactions"; prepared for the Stratospheric Workshop sponsored by the National Aeronautics and Space Administration at Harpers Ferry, West Virginia, June 4-8, 1979.

"Mechanisms of Aerosol Formation"; Scripts Institute, University of California, La Jolla, January, 1979.

"Understanding Solvation and Nucleation Through Gas Phase Clustering"; Department of Chemistry, University of California, Santa Barbara, January, 1979.

"The Importance of Heterogeneous Photochemistry in the Atmosphere"; MCA Workshop, University of California, Riverside, January, 1979.

"Statistical Mechanics of Nucleation and Early States of Aerosol Growth: Implications of Recent Experimental Findings"; invited opening address at the Gesellschaft fur Aerosolforschung (GAF) Conference, Vienna, Austria, September 26-28, 1978.

"Studies of Ion Clusters: Relationship to Understanding Nucleation and Solvation Phenomena"; (lecture) NATO Advanced Study Institute, La Baule, France, September 4-16, 1978.



"A Reconsideration of Nucleation Phenomena in Light of Recent Findings Concerning the Properties of Small Clusters, and a Brief Review of Some Other Particle Growth Processes"; to appear in the proceedings of a workshop on Thermodynamics and Kinetics of Dust Formation in the Space Medium held at the Lunar and Planetary Institute, Houston, September 6-8, 1978.

"Studies of Clustering About Ions" Relationship to Understanding Solvation, Nucleation Phenomena and Surfaces"; (seminar) Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, September 19, 1978.

"Studies of Clustering About Ions: Relationship to Understanding Solvation"; (seminar) Physical Chemistry Institute at the University of Karlsruhe, Karlsruhe, Germany, September 22, 1978.

"Bonding of Small Clusters and Relationship to Understanding the Liquid State"; (Seminar) Theoretical Chemistry Institute, University of Vienna, Vienna, Austria, September 25, 1978.

"Nucleation and Aerosol Formation"; (seminar) Chemical Systems Laboratory, Edgewood Arsenal, Maryland, July 31, 1978.

"Studies of Ion Clusters in the Gas Phase"; (seminar) Department of Chemistry, Princeton University, August 1, 1978.

"Molecular Properties of Small Clusters and Their Relationship to Understanding Nucleation Phenomena"; (with P. Holland) 175th ACS National Meeting, Anaheim, California, March 13-17, 1978.

"Chemistry of  $\text{SO}_3$ ,  $\text{NH}_2$  and  $\text{HCl}$  in the Atmosphere: Results of Recent Experiments"; Physical Symposium on Atmospheric Chemistry of the 4th Biennial Rocky Mountain Regional Meeting of the American Chemical Society (with B. D. Kay), June 5-7, 1978.

"Considerations of the Stability of Some Sulfur Compound-Water Complexes"; (with P. Holland) Physical Symposium on Atmospheric Chemistry of the 4th Biennial Rocky Mountain Regional Meeting of the American Chemical Society, June 5-7, 1978.

"Measurements of the Thermodynamic Properties of  $\text{CO}_3^-$  and  $\text{HCO}_3^-$  Hydrates and Relationship to the Negative Ion Chemistry of the Upper Atmosphere"; (with R. G. Keesee and N. Lee) Physical Symposium on Atmospheric Chemistry of the 4th Biennial Rocky Mountain Regional Meeting of the American Chemistry Society, June 5-7, 1978.

"Measurements of the Thermodynamic and Kinetic Properties of Positive Ions and Relationship to Nucleation Phenomena"; (with K. I. Peterson, D. Lindsay, P. Holland and R. G. Keesee) Physical Symposium on Atmospheric Chemistry of the 4th Biennial Rocky Mountain Regional Meeting of the American Chemical Society, June 5-7, 1978.

"Recent Advances in Experimental and Theoretical Aspects of Nucleation Phenomena"; chairman, Gordon Conference on Chemistry at Interfaces, Kimball Union Academy, New Hampshire, July 18-22, 1977.

"Chemistry of Sulfate Aerosol Formation"; Gordon Conference on Chemistry at Interfaces, Kimball Union Academy, New Hampshire, July 18-22, 1977.

"Ions in the Middle Atmosphere--Chemical Physical, and Electrical Aspects"; (convener, three sessions), Joint IAGA/IAMPA Symposium of the International Union of Geodesy and Geophysics, Seattle, Washington, August 22-September 3, 1977.

"The Influence of Heterogeneous Processes on Atmospheric Ions"; IUGG Assembly, Seattle, Washington, August 22-September 3, 1977.

"Heterogeneous Chemical Reactions and Their Importance to Aeronomy"; Special Session in honor of Professor Marcel Nicolet, IUGG Assembly, Seattle, Washington, August 22-September 3, 1977.

"Aerosols in the Atmosphere: Their Origin and Role in Heterogeneous Processes"; NASA-Langley, June 2, 1977.

"Studies of Small Clusters: Relationship to Understanding Phase Transitions and Solvation Phenomenon, (Chemical Physics seminar) Caltech, November 1, 1977.

"Clusters: Gases to Galaxies, Liquids and Life"; (Chemical Physics seminar) University of Colorado, November 4, 1977.

"Considerations of the Statistical Mechanics of Aerocolloidal Systems"; Caltech, November 30, 1977.

"Studies of Small Clusters in the Gas Phase: Their Relationship to Nucleation Phenomenon, Solvation, and Atmospheric Chemistry"; Rockwell International Science Center, December 8, 1977.

"Nucleation and Surface Formation: Theory and Experiment"; NASA-Ames, December 13, 1977.

"Ion-cluster Prenucleation Embryos: Their Formation and Properties"; Invited paper at the 173rd National American Chemical Society Meeting in New Orleans, March 21-25, 1977. (Symposium on Nucleation: Theory and Experiment.)

"Aerosols in the Atmosphere: Their Origin and Role in Heterogeneous Processes"; paper delivered at Optical Society of America meeting, Williamsburg, Virginia, December 13, 1976.

"Chemistry and Formation of Upper Atmospheric Aerosols"; (seminar) NASA-Ames, November 12, 1976.

"Nucleation and Aerosol Chemistry"; (seminar) Caltech, October 26, 1976.

"Nucleation and Aerosol Dynamics"; Oak Ridge National Laboratory, August 23, 1976.



LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

1. A. W. Castleman, Jr. (Principal Investigator)
2. Naisin Lee (Post-doctoral research associate)
3. Karen Peterson (Ph.D. student)
4. Paul Holland (Ph.D. student)
5. Robert G. Keesee (Ph.D., Department of Chemistry, University of Colorado, granted August 1979. Thesis: "A Study of Gas Phase Association Equilibria: The Clustering of Neutral Molecules onto Negative Ions")

BIBLIOGRAPHY

1. Arnold, F., J. Kissel, D. Krankowsky, H. Wieder, and J. Zähringer, J. Atmos. Terr. Phys., 33, 1169 (1971).
2. Castleman, A. W., Jr., in Physics and Chemistry of Upper Atmospheres, p. 143, Ed. B. M. McCormac, D. Reidel Publishing Co. (1973).
3. Castleman, A. W., Jr., Space Sci. Rev., 15, 547 (1974).



APPENDIX A

"Nucleation and Molecular Clustering About Ions"  
Advances in Colloid & Interface Science "Nuclea-  
tion"; A. Zettlemoyer, Ed., Elsevier Press, Oxford  
England, 10, (1979), pp. 73-128.

APPENDIX B

"The Properties of Ion Clusters and Their Relationship to Heteromolecular Nucleation"; (with P. Holland and R. G. Keese), J. of Chemical Physics, 68, 1760 (1978).



APPENDIX C

"Statistical Mechanics of Nucleation and Early Stages of Aerosol Growth: Implications of Recent Experimental Findings"; J. of Aerosol Science, 10, pp. 183-185 (1979).

#### APPENDIX D

"Studies of Ion Clusters: Relationship to Under-  
Standing Nucleation and Solvation Phenomena"; NATO  
Advanced Study Institute, "Kinetics of Ion Molecule  
Reactions," La Baule, France, September 4-15, 1978.  
Edited by Pierre Ausloos, Plenum Press, N.Y. (1979),  
p. 295.



APPENDIX E

"The Properties of Clusters in the Gas Phase: III.  
Hydration Complexes of  $\text{CO}_3^-$  and  $\text{HCO}_3^-$ ; (with R. G.  
Keese, N. Lee) J. Amer. Chem. Soc., 101, (10) 2599  
(1979).

APPENDIX F

"Atmospheric Negative Ion Hydration Derived from Laboratory Results and Comparison to Rocket-Borne Measurements in the Lower Ionosphere"; (with R. G. Keese, N. Lee) J. of Geophysical Research, 84, 3719 (1979).



APPENDIX G

"The Properties of Clusters in the Gas Phase: IV.  
Complexes of  $\text{H}_2\text{O}$  and  $\text{HNO}_x$  Clustering on  $\text{NO}_x^-$ "; (with  
N. Lee and R. G. Keese) to appear in J. of Chem.  
Phys.

#### APPENDIX H

"A Reconsideration of Nucleation Phenomena in Light of Recent Findings Concerning the Properties of Small Clusters, and a Brief Review of Some Other Particle Growth Processes"; to appear in the proceedings of a workshop on Thermodynamics and Kinetics of Dust Formation in the Space Medium held at the Lunar and Planetary Institute, Houston, Sept. 6-8, 1978, J. Astrophysics and Space Science (special issue).